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**PILOT SCALE EVALUATION OF PEROXONE FOR
TREATMENT OF CONTAMINATED GROUNDWATER**

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ABSTRACT

Advance oxidation processes (AOPs) are treatment processes that rely on the hydroxyl radical to destroy contaminants in polluted waters. Peroxone is an advanced oxidation process that utilizes the reaction of ozone and hydrogen peroxide to produce hydroxyl radicals without the requirement of ultraviolet light. The USAE Waterways Experiment Station (WES) evaluated the use of peroxone at Rocky Mountain Arsenal (RMA) for treatment of groundwater contaminated with diisopropylmethylphosphonate (DIMP) and low levels of pesticides. This evaluation was performed at RMA using a pilot-scale treatment system. Results indicate that DIMP was easily oxidized to below detection limit levels. Optimization of the process indicated that a 250 mg/l hydrogen peroxide dose in four columns plumbed in series that were all sparged with 2.2% ozonated air at a rate of 2.5 scfm.

INTRODUCTION

Rocky Mountain Arsenal (RMA) is an installation of the U.S. Army which occupies more than 17,000 acres in Adams County, Commerce City, Colorado. RMA was established in 1942 and has been the site of chemical incendiary munitions manufacturing and chemical munitions demilitarization. Following World War II, Congress approved the leasing of some portions of RMA to private industry. Agricultural pesticides and herbicides were manufactured onsite from 1947 to 1982. Past military and industrial activities at RMA have resulted in the contamination of the alluvial aquifer with various organic compounds such as diisopropylmethylphosphonate (DIMP), pesticides, and volatile organic compounds.

In support of the Office of The Program Manager Rocky Mountain Arsenal (PMRMA), the USAE Waterways Experiment Station (WES) evaluated peroxone for treatment of contaminated groundwaters using a pilot scale peroxone oxidation system. These activities focused on evaluating the feasibility of using peroxone as either a pretreatment technology for the removal of organic contaminants from the influents to existing RMA systems that do not adsorb well onto activated carbon, such as DIMP, (thus reducing the activated carbon usage as a cost saving measure) or for direct remediation of the contaminated groundwater. This paper summarizes some of the results generated by this study that was recently performed at RMA by WES during August 1994.

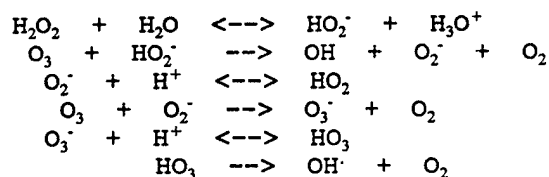
THE PEROXONE PROCESS

Chemical oxidation processes that result in the generation of the hydroxyl radical (OH[•]) have been referred to as advanced oxidation processes (AOPs) by the American Water Works Association (Langlais et al. 1991). Commercial application

of AOPs for contaminated groundwater treatment in the United States has traditionally involved UV irradiation of hydrogen peroxide, ozone, or a combination of both. In UV light based AOPs, irradiation of chemical oxidizers with ultraviolet (UV) light produces hydroxyl radicals. The hydroxyl radical is a much more powerful oxidizer than either hydrogen peroxide or ozone (Sundstrom et al. 1986).

Peroxone is an AOP that utilizes the combination of hydrogen peroxide and ozone to form the hydroxyl radical without the requirement of UV light. The results reported by Glaze et al. (1988) indicated that peroxone could effectively degrade chlorinated solvents from the groundwater. Since peroxone does not require the addition of high concentrations of chemical oxidizers and UV light, it is estimated that reductions in treatment costs as high as an order of magnitude over more traditional AOPs may be realized.

Langlais et al. (1991) present the following mechanism for the formation of the hydroxyl radical during peroxone treatment:



Discussions with French researchers indicate that some water utilities in France are currently using peroxone to treat millions of gallons per day of pesticide contaminated groundwater (Personal communication with Dr. Marcel Dore, University of Poitiers 1992). The French researchers claim that treatment costs are on the order of \$0.05 per 1,000 gallons treated. Glaze et al. (1988) performed laboratory scale studies on the ability of peroxone to remove TCE and tetrachloroethylene (PCE) from a contaminated groundwater. The results proved positive enough to warrant subsequent pilot-scale evaluations (Aieta et al. 1988). Both the bench and pilot studies concluded that the reaction rate of TCE and PCE was increased by factors of 1.8 to 2.8 and 2.0 to 6.5, respectively, as opposed to those achieved by ozonation alone. Apparently, TCE was reactive toward ozone alone as well as the hydroxyl radicals formed; PCE was only reactive toward the radical species. Both studies indicated that a hydrogen peroxide-to-ozone ratio between 0.25 and 0.5 was optimal for removing TCE and PCE from the groundwater studied. The Metropolitan Water District of Southern California (1991) evaluated peroxone using pilot scale systems for treatment of 2-methylisoborneol (MIB) and trans-1,10-dimethyl-trans-9-decanol (geosmin). The District concluded that optimum hydrogen peroxide-to-ozone ratios for removal of MIB and geosmin was 0.1 to 0.2. They further conclude that peroxone was better for removal of MIB and geosmin than ozone alone due to increased hydroxyl radical production.

Researchers at the WES have recently developed a numerical model for estimating the steady-state hydroxyl radical concentrations in peroxone systems (under publication). The hydroxyl radical production and destruction mechanisms as described by the WES model are presented in the equation below,

$$[\text{OH}^\cdot] = \frac{(2k_6[\text{O}_3][\text{H}_2\text{O}_2]K_{\text{H}_2\text{O}_2}[\text{H}^+]^{-1})}{(k_4[\text{O}_3]) + (k_5[\text{H}_2\text{O}_2]) + (k_X[\text{X}]) + (k_S[\text{S}])}$$

where, X = Target Contaminant
S = Radical Scavengers
K and k = Rate Constants

The above model indicates that there are numerous chemical reactions that may occur that can remove hydroxyl radical species from a reactor fluid. Only those reactions that either result in production of the radical (shown in the numerator of the equation) and/or the destruction of the contaminant are considered

beneficial (the X term in the denominator). The other reactions have an adverse impact on reaction kinetics due to the scavenging of radicals that would have been available for contaminant destructive reactions.

Based on radical production/reaction chemistry, WES has identified three predominant scavenging reactions that will most likely govern reactions within traditional AOP reactor systems when treating contaminated groundwaters. These are reactions with bicarbonate/carbonate ions, reduced cations (i.e. iron), and excessive amounts of primary oxidizers (i.e. ozone and hydrogen peroxide). Of particular interest to this study is that too much ozone or hydrogen peroxide may be added to an AOP system. Usually obtaining excessive amounts of ozone is difficult because ozonation is mass transfer limited (gas to water transfer). However, introduction of hydrogen peroxide (a liquid) is much easier and is likely a potential scavenging source in AOPs. There is an optimum dose for each oxidizer and optimum stoichiometric mass-to-mass ratios for those AOPs utilizing both oxidizers, such as peroxone. Some of the data presented in this report serve as excellent examples of these interactions.

STUDY BACKGROUND AND OBJECTIVES

In 1993, the WES evaluated the potential for three AOPs for removal of DIMP from RMA groundwaters. AOPs evaluated include UV/hydrogen peroxide, UV/ozone, and peroxone. These efforts were accomplished using one liter bench reactors. The results from this effort indicate that any time UV light was added to the hydrogen peroxide system or ozone, extremely rapid degradation rates were observed. Although the peroxone system did not have as rapid degradation as the UV based processes, appreciable degradation of DIMP was observed. The peroxone bench study indicated that hydraulic residence times (HRTs) in excess of 30 minutes will required to remove DIMP to below detection limit levels (BDLLs). Reaction of DIMP with the parent oxidizers used in the bench study, ozone and hydrogen peroxide, were found not to be reactive toward DIMP. This indicates that the primary removal mechanism for DIMP was the hydroxyl radical and/or photolysis.

The results of the bench studies for DIMP removal were considered very promising. The UV based systems had more rapid DIMP degradation rates than the peroxone systems. Unfortunately, UV based systems are more expensive than peroxone systems and are very sensitive to influent UV transmissivity. UV based systems are also susceptible to fouling of the quartz tubes which house the UV lamps. Peroxone oxidation is estimated to cost as low as an order of magnitude lower than traditional UV based AOPs and are not susceptible to problems associated with iron fouling or poor influent UV transmissivity. Therefore, further evaluation of peroxone oxidation for DIMP removal to BDLLs was initiated using a WES developed and constructed pilot scale system with the objective of evaluating the two application scenarios discussed above.

EQUIPMENT DESCRIPTION

The peroxone oxidation pilot system (POPS) used in this study was designed and constructed by the WES. The system had the capability of evaluating influent flowrates ranging from 0.5 to 15 gallons per minute (gpm). For this study a constant flowrate of 0.9 gpm was used. Figure 1 presents an illustration of the POPS unit. The system was plumbed in a countercurrent flow mode with the hydrogen peroxide dosed influent flowing downward and the ozonated gas flowing upward through the columns. Hydrogen peroxide doses was mixed with the influent using an in-line vortex mixer.

The POPS unit used a 3 lbs. per day OrecTM ozone generator capable of producing a continuous stream of air containing up to 2.5 percent ozone (wt/wt). Ozonated air was introduced into four 6 inch ID by 14 foot high, all-glass columns via ceramic spargers located on the column bottoms. A central data logging, system control unit comprised of a Gateway 486, 200 Mbyte, 50 MHz computer was used for on-screen operations analysis of process operations which was used for system operation and real-time data logging. Hydrogen peroxide was

introduced into the influent stream using a metering pump to precisely dose the peroxone system with hydrogen peroxide of varying strengths (depending on the target dosage). Two IN-USATM ozone monitors were used with the system for gas phase analysis. One unit was used to monitor ozone generator output in percent ozone (wt/wt). The other unit had multi-port capability for analyzing air phase ozone concentrations at various sampling points including column headspace, pre- and post-ozone destruct unit, and ambient air. An IN-USATM in-line ozone monitor with multi-port capability will be used for analyzing residual ozone levels in the effluents exiting any of the four columns. Ozone exiting the columns that was not transferred into the column influents was passed through an ozone destruct system to prevent release of ozone into the ambient air. DIMP is not volatile so there were no concerns about DIMP loss via volatilization during ozonation.

APPROACH

RMA groundwater was used as the influent for this study. This influent contains DIMP at approximate levels that approach 100 ppb. The POPS unit was operated at a constant ozone feed of 2.2% ozone at a flowrate of 2.5 scfm with varying hydrogen peroxide doses into the influent added prior to entry into the first column. Influent was added to the system at a constant flowrate of 0.9 gpm which represented an approximate system hydraulic residence time (HRT) of 90 minutes (23 minutes per column). Analytical samples for DIMP analysis using gas chromatography were collected periodically after each POPS column in precleaned all-glass, one liter sample bottles. DIMP analyses was performed by the RMA Analytical Laboratory. Ozone and hydrogen peroxide concentrations exiting the columns were also recorded.

RESULTS

A DIMP concentration of BDDLs (<1.78 ug/l) was selected as a target treatment goal for comparison of process formulation performance. Tables 1 through 3 summarize the results of the POPS runs for hydrogen peroxide doses of 100 mg/l, 250 mg/l, and 500 mg/l, respectively. These data indicate that the 250 mg/l dose (Table 2) had slightly more rapid removal kinetics than the 100 mg/l dose (Table 1). The addition of 500 mg/l (Table 3) had a slight inhibitory effect on DIMP removal. The mechanism of rate inhibition is believed to be the reaction of hydroxyl radicals with the excessively high amounts of hydrogen peroxide present in the reactors (Table 3). The WES steady-state hydroxyl radical model for peroxone presented earlier illustrates how excessive amounts of either oxidizer may hinder contaminant degradation rate. In fact, the rationale for the 100 mg/l hydrogen peroxide dose to perform slightly worse than the 250 mg/l was attributed to excessive amounts of ozone present in the column which reacted with some of the hydroxyl radicals produced because of the limited amounts of hydrogen peroxide present in the columns. This effect is also illustrated in the steady-state hydroxyl radical model for peroxone systems.

In summary, all three hydrogen peroxide doses were capable of meeting the target treatment goal of BDDLs. The 100 and 250 mg/l doses reached target levels within an HRT range of greater than 23 minutes, but less than 46 minutes. This HRT supports the results of the WES bench study which predicted a HRT of at least 30 minutes would be required to meet the BDDL target. The 500 mg/l dose appeared to hinder DIMP oxidation reactions due to the excessive amounts of hydrogen peroxide present. This hindering effect is explained by the numerical model for steady-state hydroxyl radical concentrations in peroxone systems.

FURTHER EFFORTS

The results of this study were considered very encouraging. Further analysis of the applicability of the peroxone process at RMA is on-going. The 250 mg/l hydrogen peroxide dose appeared to be the optimum process formulation for the conditions evaluated to date. However, WES has generated additional data using varying ozone doses and flowrate. The steady-state [OH] model predicts that reduced ozone and hydrogen peroxide doses may provide similar treatment

efficiencies at significantly reduced treatment costs due to decreased oxidizer demands. These data are currently being evaluated and will be published when available.

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Table 1. 100 mg/l Hydrogen Peroxide Dosed POPS Run

Sample Location*	Cummulative HRT, minutes	Water [H ₂ O ₂], mg/l	Water [O ₃], mg/l	Water [DIMP] ug/l
Influent	0	100	0	70
Column 1	23	80	0.6	14
Column 2	46	30	BDL	BDL
Column 3	69	1	0.3	BDL
Column 4	93	0.2	BDL	BDL

* - Column data based on samples collected directly after exiting the column
 BDL - Below detection limit (0.1 mg/l for oxidizers and 1.78 ug/l for DIMP)

Table 2. 250 mg/l Hydrogen Peroxide Dosed POPS Run

Sample Location*	Cummulative HRT, minutes	Water [H ₂ O ₂], mg/l	Water [O ₃], mg/l	Water [DIMP] ug/l
Influent	0	250	0	65
Column 1	23	200	1.7	10
Column 2	46	125	1.2	BDL
Column 3	69	50	0.4	BDL
Column 4	93	0.2	BDL	BDL

* - Column data based on samples collected directly after exiting the column
 BDL - Below detection limit (0.1 mg/l for oxidizers and 1.78 ug/l for DIMP)

Table 3. 500 mg/l Hydrogen Peroxide Dosed POPS Run

Sample Location*	Cummulative HRT, minutes	Water [H ₂ O ₂], mg/l	Water [O ₃], mg/l	Water [DIMP] ug/l
Influent	0	500	0	60
Column 1	23	500	2.0	14
Column 2	46	350	1.9	3.7
Column 3	69	275	2.0	BDL
Column 4	93	200	1.6	BDL

* - Column data based on samples collected directly after exiting the column
 BDL - Below detection limit (0.1 mg/l for oxidizers and 1.78 ug/l for DIMP)